R.H.G.

AIR POLLUTION 1976

CD Doc #10

R POD #9 (-)

C. DUTRA FILES

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Interoffice Communication

To R. D. Gamblin

From J. E. Cearley

Date January 2, 1976

Subject Status of Chemical Exposure Abatement Program

A. CURRENT STATUS

The initial comprehensive monitoring of the first group of chemicals considered as "high risks" has been completed, and we now know which of these chemicals have the greatest potential for employee exposure to unacceptable levels. Additional chemicals have been added to the monitoring list as the sampling program progressed. The permissible exposure levels of the chemicals that have been monitored thus far are presented in Table 1, and the monitoring results (June-November, 1975) are shown in Table 2. The sampling techniques and analytical methods being used for the various chemicals are depicted in Table 3.

The results of the sampling and analyses for the chemicals monitored thus far indicate time-weighted employee exposures are below the action level. The primary exposure problems encountered have been the short-term high level exposures that exceed the ceiling and/or maximum peak concentrations, i.e., methyl chloride, hydrogen chloride, benzene, and ammonia. Corrective measures to reduce these short-term high level exposures to acceptable concentrations are either in the planning stages or are being carried out (Table 4).

B. CHEMICALS WITH EXPOSURE-REDUCTION REQUIREMENTS

1. Ammonia

The areas of the plant having the greatest potential for employee exposure to ammonia are around the ammonium hydroxide storage tank located in Section 500 of the Alcohol Unit and the ammonium hydroxide storage and day tank located at the Holding Pond.

In Section 500, high ammonia exposures occur only when the ammonium hydroxide storage tank is being filled by tank truck. The storage tank vents to grade (open sewer); and while being filled, there is considerable quantities of ammonia vapors emitted to the atmosphere. Previous area monitoring showed levels in excess of the ceiling limitation of 50 ppm for 5 minutes. In order to reduce the exposure levels, the storage tank vent will be rerouted to the acid holding pit, with the discharge being located below the surface of the water; this will scrub out a significant portion of the emissions. In addition, a hood with a vent to the atmosphere will be installed over the acid holding pit, which will reduce employee exposure to emissions from the pit.

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At the holding pond, ammonia is added to the waste water as a nutrient for the biological organisms in the Aerated Lagoons. Personal monitoring indicated expsoure levels were below the action level, which was because employees filling the day tank position themselves upwind so as to avoid the ammonia emissions. However, area monitoring showed levels in excess of the action level. In order to reduce the ammonia emissions, the vent and discharge lines from the ammonium hydroxide storage and day tanks were extended so that the outlets were located below the water level. We have not been adding ammonium hydroxide for several months, so we have not been able to monitor these operations since the corrections were made. As soon as we begin nutrient additions, monitoring will be conducted.

2. Phosgene

The potential for phosgene exposure exists in the Methyl Chloride Unit; phosgene is present in the hydrogen chloride feed from Olin when there is an upset in their system. We recently had two laboratory personnel exposed to high phosgene levels while working on the mobile GC monitor located at the Methyl Chloride Unit; this occurred when the unit was being started up.

In order to prevent additional employee exposure, a phosgene analyzer has been installed on the HCl stream at the Methyl Chloride Unit. The instrument has performed very well so far. In addition, Olin will install an identical analytical instrument at their location to monitor the HCl line to the Chemical Plant. With these two instruments in operation, we should not have any more "surprise" high level exposures.

An additional safeguard is the fact that we currently analyze methyl chloride 4 to 5 times daily. Our calculations indicate that a phosgene level of 200 ppm would be necessary for the potential to exist for employee exposure to levels in excess of the ceiling limitation. In addition, an employee would have to be exposed to approximately 5000 ppm of methyl chloride with a phosgene level of 10 ppm in order to be exposed to the ceiling limitation. With the product sampling program and the HCl feed monitoring, we should be able to prevent employee exposure to unacceptable phosgene levels.

3. Hydrogen Chloride

The primary exposure problem with HCl is when personnel collect samples at the Methyl Chloride Unit for routine analysis. The sample bombs are vented directly to the atmosphere in the immediate area of the employee. A design for a sampling system that will reduce exposure to an acceptable level has been completed and issued.

4. Benzene

Personal monitoring of Ethylene Unit employees indicated the time-weighted average levels were below the action level of 5 ppm. However, fixed point monitoring has indicated levels in excess of the ceiling limitation for the Quench Water Settler and a sewer vent located at the base of the light aromatics distillate tower. Of these two sources of emission, the Quench Water Settler is by far the major source of benzene exposure. In addition to these emission source points, preliminary sampling has indicated potential exposure problems with the 201 first stage knockout drum drain to the sewer.

Another potential source of benzene exposure is the API separator located at the Holding Pond; this separator receives discharges from the Alcohol and Ethylene Units oily water sewers. The Ethylene discharge includes discharges from the Quench Water Settler, thereby creating the potential for benzene emissions. The mobile GC analyzer has been relocated at the API separator, and monitoring will be conducted to determine benzene levels.

The initial intensive monitoring program for benzene will be completed by January 1, 1975. As soon as all the data is evaluated, recommendations will be made as to the corrective actions needed to reduce benzene exposures to an acceptable level.

5. Ethylene Oxide

Personnel exposures to ethylene oxide have been well below the action level. One potential exposure problem picked up by area monitoring was a vent off the ETO reactor that discharges to an open ditch. This vent is used to blowdown and purge the reactor at the end of each run.

A steam-traced knockout pot with a vent 10 feet above the ETO Building will be installed (cost estimate of $1,250). Since the emissions are intermittent and of a short duration, this system will be adequate. The OVA instrument will be used to periodically monitor the EO system in order to detect any leaks; this is important since ethylene oxide cannot be detected by smell until concentrations are up around 700 ppm.

6. Methyl Chloride

Methyl chloride is the chemical that has presented the greatest problem as far as employee exposure is concerned. Although personal monitoring has indicated exposure levels below the action level, grab samples and mobile GC analyses indicated occasional high levels that exceed the ceiling limitation. The major problem areas where exposures to concentrations in excess of the 300 ppm maximum peak limitation are possible are:

1. Bleeding the D-7 compressor suction knockout drum.
2. Bleeding D-8 oil wash knockout drum.
3. Additions of caustic to T 11-20.
4. Collection of sample bombs for laboratory analysis - venting to the atmosphere occurs.
5. Loading of tank cars - venting to the atmosphere.
6. Location of vents on low and high side of compressor piston rod seal.
7. Numerous atmospheric emergency vents throughout the unit.
8. Vents and bleeders into open sewer.
9. Relief valves in the unit.
10. Location of chiller vent stack.

A design for reducing emissions when collecting samples for lab analysis has been completed and is being reviewed. The remaining items have been assigned to Process Engineering, and as soon as the designs are complete (February, 1976), cost estimates will be made.

The OVA instrument was used recently to go through the unit and locate leaking valves, seals, etc. During the last turnaround, the major leaks were repaired, thereby reducing fugative emissions. We recently submitted an AFE for the purchase of an OVA instrument for the Methyl Chloride Unit so that operations can routinely check for leaks.

C. PROPOSED SCHEDULE FOR 1976-1977 PERSONNEL MONITORING PROGRAM

The proposed schedule for monitoring of chemicals in the plant for the next two years (1976-1977) is present in Table 5. We will attempt to adhere to this schedule, although proposed and finalized standards for various chemicals by OSHA may change the priority of our sampling schedule. Our existing manpower prevents us from moving ahead any faster than what is proposed; therefore, it will take us a minimum of two years to look at all of the more obvious chemical exposures.

The general format that will be followed in our sampling program is as follows:

1. In all monitoring, samples representative of each job classification for all shifts will be collected. We will attempt to monitor at least 50% of the employees in each operation or process. In addition to operations personnel, maintenance employees will be monitored, particularly during turnaround and major repair work where the potential for high level exposures is greatest.

2. Monitoring of an operation or process will be repeated at least monthly when the concentration has been found to exceed the action level.

3. If the concentrations exceed the recommended TLV standards, monitoring will be conducted at biweekly intervals until two consecutive surveys indicate the adequacy of the control measures taken.

4. Samples will be collected semi-annually for those chemicals below the action level and considered as "high risk," i.e., methyl chloride, hydrogen chloride, ethylene oxide, and benzene. Other chemicals below the action level will be monitored every 12 to 18 months, depending on the chemical's toxicity and the potential that exists for employee exposure.

5. For those chemicals that have relatively high established TLV values, and we are assured exposures do not approach the action levels, written determinations will be made and placed in our files. Some of the chemicals currently believed to fit this category are butadiene, pentane, LPA solvent, propane-propylene, and various raw materials and supplies, such as various Nalco products.

   We currently are considering placing phosgene in this category, since a phosgene analyzer has been installed on the HCl feed line and Olin Chemical is in the process of installing an analyzer at their facility. In addition, we analyze the methyl chloride product four to five times daily, and we know how much phosgene must be present in the product for the potential of exposure to unacceptable levels to exist.

6. As time permits, training programs will be developed for the various chemicals. We realize the importance of training programs, but our manpower is such that we are unable to develop this area as rapidly as we would like.

7. Routine plant inspections (one to two times per month) will be made to evaluate housekeeping activities and work habits in the various units.

8. Where feasible, engineering design changes will be made to reduce employee exposures to acceptable levels. Where engineering controls are not feasible, personal protective equipment will be utilized.

The Chemical Plant will adhere to this format as much as possible, although proposed and finalized OSHA regulations for various chemicals may require changes in our current schedule. In addition, there are no established sampling and analytical procedures for some of the chemicals to be monitored, and we may run into difficulties here.

D. COSTS OF CORRECTIVE MEASURES REQUIRED FOR EXPOSURE REDUCTIONS

At the present time, we do not have a good feel for the cost of corrective measures that will be required to reduce employee exposures to acceptable levels. It appears that the major expenditure will be for the Methyl Chloride Unit. The design work for reducing emissions in the Methyl Chloride Unit is scheduled to be completed by February 1, 1976; once the design has been reviewed and approved, cost estimates will be made.

E. MONITORING EQUIPMENT

In order to adequately carry out the monitoring program, we will need some additional monitoring equipment (Table 6). A tentative estimate of the costs of sampling equipment that will definitely be needed in 1976 is approximately $4,000. Additional analytical equipment that may be required has been included in Table 6 as 1977 Capital Budget items.

J. E. Cearley

J. E. Cearley

mbr

Enclosures

cc + encs: RAC RHG DDZ DDP

TABLE 1

Chemical	8-Hour Time Weighted Average	Action Level	Acceptable Ceiling Concentration	Acceptable Maximum Peak Above the Acceptable Ceiling Concentration for an 8-Hour Shift
Methyl Chloride	100 ppm	50 ppm	200 ppm (5 minutes in every 3 hrs.)	300 ppm
Methanol	200 ppm	100 ppm	-	-
C Hydrogen Chloride	-	2.5 ppm	5 ppm	-
C Phosgene	-	0.025 ppm	0.05 ppm	-
Ethylene Oxide	50 ppm	25 ppm	-	-
Benzene	10 ppm	5 ppm	25 ppm (10 minutes)	50 ppm
Sulfuric Acid	1 mg/m^3	0.5 mg/m^3	-	-
Butanol	50 ppm	25 ppm	-	-
Hexanol	No Established TLV			
Ethanol	1000 ppm	500 ppm	-	-
Acetic Acid	10 ppm	5 ppm	-	-
C Ammonia	-	25 ppm	50 ppm (5 minutes)	-
Carbon Monoxide	50 ppm	25 ppm	-	-
Vinyl Chloride	1 ppm	0.5 ppm	5 ppm (15 minutes)	-
Chlorine	1 ppm	0.5 ppm	-	-
Calcium Hydroxide	2 mg/m^3	1 mg/m^3	-	-
*Asbestos	Two Fibers (> 5 micrometers)/cc of air			

*Monitoring handled by Safety

TABLE 1 (CONT'D.)

NOTE: 1. Acceptable Ceiling Concentration (C) - Those chemicals preceded by a "C" shall at no time exceed the ceiling value given for that material in the table, unless a maximum peak value is designated.

2. 8-Hour Time Weighted Average - An employee's exposure to a designated chemical shall not exceed the 8-hour time weighted average in any 8-hour work shift of a 40-hour work week.

3. Action Level - The action level is one-half the TLV; if exposures are below this level, then no further action is required, other than monitoring every 6 months. However, if exposures are greater than the action level, then more frequent monitoring is required (generally montnly), medical surveillance must be implemented, control measures must be improved, and various other requirements are necessary.

4. Maximum Peak Above Acceptable Ceiling Concentration - The ceiling standard may be exceeded for short periods (generally 5 to 30 minutes) up to a concentration defined as "acceptable maximum peak above the acceptable ceiling concentration for an 8-hour shift."

TABLE 2

Chemical	< Action	> Action Level < Max Permissible Level	> Max Permissible Level	Method
Methyl Chloride	4991	823	165	(1)
	12	0	0	TWA
	50	8	12 (6 above max peak)	Grab
Methanol	6540	228	175	(1)
	11	0	0	TWA
	101	1	0	Drager
Hydrogen Chloride	120	0	1	Drager
	4	0	1	TWA
Sulfuric Acid	6	0	0	TWA
Ammonia	9	0	0	TWA
	32	6	7	Drager
	10	4	4	Area-Monitoring
Acetic Acid	13	2	3	Drager
Benzene	2087	348	1058	(1)
	116	3	1	Drager
	11	0	0	TWA
Ethylene Oxide	2398	5	9	(1)
	12	0	0	TWA
	6	2	2	Grab
Chlorine	127	0	0	Drager
Carbon Monoxide	72	1	0	Drager
Hexanol	4539[a]	-	-	(1)
	12	0	0	TWA
Ethanol	5290	0	0	(1)
	12	0	0	TWA
Butanol	4470	441	379	(1)
	12	0	0	TWA
Vinyl Chloride	11	0	0	TWA
Phosgene	99[b]	0	0	Drager

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a-Samples averaged 1.0 ppm

b-All samples less than .15 ppm

*(1) Multi-Sample Point Environmental GC
TWA - Time Weighted Average
Grab - Grab Samples
Drager - Drager Tubes

TABLE 3

HAZARDOUS MATERIAL	SAMPLE COLLECTION	ABSORBENT	DESOR.	REFERENCE	DETECTION	REMARKS
Methyl Chloride	1. Sipin SP-3	Carbosieve-B Pri-80/100 mesh 400 mg Sec-45/60 mesh 100 mg	Bendix Flasher 300°C	LCCP	FID, 8', 1/8" Poropak Q-S (100/120 mesh) 100°C	Results hampered by high humidity (rain), Flash tube prior to use.
	2. Multi-Sample Point Environmental GC				FID, 10', 1/8" Carbowax 1500 (10% on W) 80°C	Area monitoring
	3. OVA Century 98 Portable GC				FID	Leak Detection and Peak Concentration Studies
Ethylene Oxide	1. Multi-sample Point Environmental GC				FID, 10', 1/8" Carbowax 1500 (10% on W) 80°C	Area monitoring, Note: Poor results by Sipin pumps and air bags
Methanol	1. Sipin SP-3	Silica Gel (30/60 mesh) 400 mg - primary 100 mg - backup	Water	LCCP-NIOSH S59-1	FID, 8', 1/8" Propak QS (100/120 mesh) 115°C	85% Recovery, plan to use flasher after preliminary study
	2. Multi-Sample Point Environmental GC				FID, 8', 1/8" Carbowax 1500 (10% on W) 80°C	Area monitoring
	3. Drager Tubes					Poor sensitivity
Hydrochloric Acid	1. Midget Impingers	.01N Sodium Hydroxide		AIHA	Colorimetric-thiocyanate	Minimum detection is .5 ppm in 15 minute sample. Plan to investigate Miran IR for peak
	2. Drager Tubes					
Sulfuric Acid	1. Midget Impingers	1% Sodium Hydroxide		AIHA	Colorimetric-Barium Sulfate	Minimum detection is .2 mg/m^3
Phosgene	1. Drager Tubes					Poor sensitivity
Benzene	1. Sipin SP-3	Calgon PCP 12x30 Charcoal, 500 mg	Carbon Disulfide		FID, 20', 1/8" DEGS (12% on P)(60/80 mesh) 65° for 6 minutes to 140° at 8° per minute.	Run by VCM - Paul Fetzer
	2. Multi-Sample Point Environmental GC				FID, 8', 1/8" SE-30 90° (6% on 100/120 mesh varoport 30)	Area monitoring
	3. Drager Tubes					
	4. OVA Century 98 Portable GC				FID	Leak detection and peak concentration studies
Vinyl Chloride	1. Sipin SP-3	Calgon PCP 12x30 Charcoal, 500 mg	Carbon Disulfide		FID, 20', 1/8", DEGS (12% on P, 60/80 mesh) 65° for 6 minutes to 140° at 8° per minute	Run by VCM - Paul Fetzer
Ethanol, Butanol, Hexanol	1. Sipin SP-3	Calgon PCP 12x30 Charcoal, 300 mg - Pri Sec-100 mg	Carbon Disulfide containing 1% 2-Butanol and .2% Dodecanol	LCCP-NIOSH S56-1&S66-1	FID, 10', 1/8" FFAP (10% on 60/80 mesh W)	6+ alcohols can also be determined Recovery - Ethanol - 55-80% Butanol - 72-88%
	2. Multi-Sample Point Environmental GC				FID, 8', 1/8", SE-30 (6% on 100/120 mesh varoport 30) 90°	Area Monitoring
	3. OVA Century 98 portable GC				FID	Leak Detection
Ammonia	1. Midget Impinger	0.1 N Sulfuric Acid		NIOSH	Colorimetric-Nessler Reagent,	Minimum detection .2 ppm in 5 minute sample
	2. Drager Tubes					
[illegible] Acetic Acid	1. Drager Tubes					

TABLE 4

CORRECTIVE MEASURES FOR REDUCING CHEMICAL EXPOSURES

CHEMICAL	UNIT	MAJOR SOURCE(S) OF EXPOSURE	CORRECTIVE ACTION	COMPLETION DATE	STATUS
Ammonia	Waste Water Holding Pond (Nutrient Addition)	Filling of Ammonium Hydroxide Storage and Day Tank; Discharge for Day Tank	Discharge and vent lines extended to below the water level of the influent waste water		Complete
	Alcohol	Filling of Ammonium Hydroxide Storage Tank - Vents to Atmosphere	Vent line rerouted to Acid Holding Pit and extended to below the water level	2-1-76	Work rescheduled due to priority
HCl	Methyl Chloride	Sampling HCl Feedstock	Redesign sampling system - enclosed loop	4-1-76	Design issued 12-30-75
Ethylene Oxide	Ethoxylation	Vent used to Blowdown ETO Reactor at Grade Level	Install knockout pot and vent to atmosphere	2-1-76	Original cost estimate was high; project redesigned - work rescheduled
Methyl Chloride	Methyl Chloride	Loading of Tank Cars - Venting to Atmosphere Bleeding of Knockout Drums Sample Bomb Collections Additions of Caustic to T 11-20 Various Vents, Relief Valves, and Bleeders	Designs currently underway to provide engineering changes for reduction of emissions	Design to be complete by February 1, 1976	Assigned to Process Engineering for design work
Benzene	Ethylene	Quench Water Settler Vent off of Light Aromatics Distillate Tower	Monitoring for benzene has recently been completed and the data is being evaluated.	Recommendations by 1-31-76	Recommendations as to corrective action needed being prepared
	Ethylene Offsites	API Separator at Waste Water Holding Pond Manholes along Ethylene Oily Water Sewer Line	Recommendation as to corrective measures needed are being prepared		

TABLE 5

CHEMICAL	UNIT	METHOD
	January 1 - February 15, 1976	
Methyl Chloride	Methyl Chloride	1
Methanol	Methyl Chloride, Ethylene	1
Hydrogen Chloride	Methyl Chloride	1
Sulfuric Acid	Methyl Chloride, Alcohol, Cooling Towers	1
Ethylene Oxide	Ethoxylation	1
	February 15 - May 1, 1976	
Benzene	Ethylene, Ethylene Offsites	1
Vinyl Chloride	Ethylene	1
Ammonia	Alcohol, Ethylene Offsites	1
Hydrogen Sulfide	Normal Paraffin	1
Butanol	Alcohol	1
Ethanol	Alcohol	1
Hexanol	Alcohol	1
	May 1 - June 1, 1976	
Carbon Monoxide	Alcohol	1
Chlorine	Ethylene and Alcohol Cooling Towers	1
Calcium Hydroxide	Steam Plant	1
Acetic Acid	Ethoxylation	1
Chromate	Alcohol Cooling Tower	1
Mercury	East and West Shops	1
	June 1 - August 1, 1976	
Hexane	Alcohol	1
Phosphoric Acid	Ethylene Offsites, Ethoxylation	1
Caustic	Ethylene, Methyl Chloride	1
Sulfur Dioxide	Steam Plant	1
Methyl Chloride	Methyl Chloride	1
Hydrogen Chloride	Methyl Chloride	1
Ethylene Oxide	Ethoxylation	1
Benzene	Ethylene, Ethylene Offsites	1
	August 1 - October 31, 1976	
Sulfur Dioxide	Normal Paraffin, Methyl Chloride	1
TBC	Ethylene	1
TPT	Alcohol	1
Nalco Products	Ethylene, Ethylene Offsites, Normal Paraffin	1
Methyl Chloride	Methyl Chloride	2
Methanol	Methyl Chloride	2
Ethylene Oxide	Ethoxylation	2
Benzene	Ethylene, Ethylene Offsites	2
Vinyl Chloride	Ethylene	2

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TABLE 5 (CONT'D.)

CHEMICAL	UNIT	METHOD
	November 1 - December 31, 1976	
Butanol	Alcohol	1, 2
Ethanol	Alcohol	1, 2
Hexanol	Alcohol	1, 2
Total Hydrocarbons	ATE Quench, Waste Water Holding Pond	2
Merox	Ethylene, Ethylene Offsites	1
	January 1 - March 31, 1977	
Methyl Chloride	Methyl Chloride	1
Methanol	Methyl Chloride	1
Hydrogen Chloride	Methyl Chloride	1
Sulfuric Acid	Methyl Chloride, Cooling Towers	1
Ethylene Oxide	Ethoxylation	1
Benzene	Ethylene, Ethylene Offsites	1
Vinyl Chloride	Ethylene	1
Sulfur Dioxide	Ethylene	1
	April 1 - June 30, 1977	
Ammonia	Alcohol, Ethylene Offsites	1
Hydrogen Sulfide	Normal Paraffin	1
Butanol	Alcohol	1
Ethanol	Alcohol	1
Hexanol	Alcohol	1
Sulfur Dioxide	Alcohol	1
Carbon Monoxide	Alcohol	1
Alumina	Alcohol	1
	July 1 - September 30, 1977	
Methyl Chloride	Methyl Chloride	1
Ethylene Oxide	Ethoxylation	1
Benzene	Ethylene, Ethylene Offsites	1
Vinyl Chloride	Ethylene	1
Chlorine	Ethylene and Alcohol Cooling Towers	1
	October 1 - December 31, 1977	
Caustic	Methyl Chloride, Ethylene, Ethylene Offsites	1
Phosphoric Acid	Ethoxylation, Ethylene Offsites	1
Hexane	Alcohol	1
Sulfur Dioxide	Normal Paraffin, Methyl Chloride	1
Calcium Hydroxide	Steam Plant	1
Acetic Acid	Ethoxylation	1

TABLE 5 (CONT'D.)

NOTE: Monitoring for asbestos will be conducted whenever employees come in contact with the material, which is only when old insulation is removed. Monitoring is handled by Safety.

1. Personal Dosimetry

2. Mobile Multi-Point GC

TABLE 6

MONITORING EQUIPMENT

EQUIPMENT ON HAND	NUMBER	COST
Sipin S-P3 Pump	4	$1,600.00
Bendix C-115 Pump	2	On Loan From VCM Plant
*Century Organic Vapor Analyzer (OVA)	1	$4,000.00
MSA Pump	1	-
Bendix Flasher (For use with Lab. G.C.)	1	$ 700.00

*One additional OVA on order for Methyl Chloride Unit

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EQUIPMENT NEEDS DURING FIRST QUARTER 1976	NUMBER	COST
Sipin S-P3 Pump	4	$1,600.00
Sipin S-S1 Pump	2	$ 800.00
Bendix C-115 Pump	2	$1,200.00

1977 CAPITAL BUDGET ITEMS	NUMBER	COST
Laboratory G.C. Analyzer	1	$8,500.00
Miran-II Infrared Portable Analyzer	1	$6,500.00
MDA Personal Monitoring System		
a) Pumps	4	$3,000.00
b) Analyzer	1	$2,500.00
Miscellaneous		$5,000.00